# REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188



| 1. AGENCY USE ONLY (Leave blank) | 2. REPORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|---|
| | 2/24/97 | FINAL REPORT 10/1/93 - 12/31/96 |

**4. TITLE AND SUBTITLE**
AEROSOL PROPERTIES AND DYNAMICS IN THE MARINE BOUNDARY LAYER, "Real Time Measurement of Oceanic Ammonia Flux"

**5. FUNDING NUMBERS**
Grant No.:
N00014-92-j-1388

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**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

**11. SUPPLEMENTARY NOTES**

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**
Unlimited

19970310 010

**13. ABSTRACT** (Maximum 200 words)

This grant incorporated two proposals that have three major efforts. These included support for our participation in and analysis of ASTEX aircraft data, a related measurement program at a coastal site in Hawaii and a separate proposal funded to develop an ammonia flux detector for the real time study of ocean-atmosphere fluxes. In pursuing these objectives, we demonstrated that modeling of aerosol microphysics was successful at establishing radiative closure with in situ aircraft measurements within about 20%. We also showed that fine particle sulfate dominates short wavelength extinction for pollutant aerosol over the Atlantic and demonstrated that soot aerosol in European pollution was internally mixed with sulfate and contributed about 15% to the total column extinction. In related work we demonstrated that a Lagrangian aerosol experiment was feasible and that the dominant influence on aerosol evolution in a non-precipitating system was dilution through entrainment from the free troposphere. This included a decoupled boundary layer model that established constraints on entrainment through the inversion and mixing. Our most recent activities demonstrated that a continuous ammonia flux detector is feasible and can be deployed from ship under typical open ocean conditions.

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| Atlantic pollution aerosol; Radiactive/optical closure; Ammonia flux; Lagrangian evolution of aerosol | 6 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | Unclassified | Unlimited |

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std. 239-18
298-102

**ONR Final Report for grant N00014-92-j-1388**
**October 1, 1993 to December 31, 1996**

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# AEROSOL PROPERTIES AND DYNAMICS IN THE MARINE BOUNDARY LAYER

Supplemented 1994 additional funds in response to proposal
**"Real Time Measurement of an Oceanic Ammonia Flux"**

## LONG TERM GOALS

Our intent is to establish an improved understanding of the properties and factors that control the physicochemistry of marine aerosol and the implications for the optical properties of the marine aerosol. These include issues related to the source, transformation and evolution of aerosol physicochemistry with particular interest in sulfate, ammonia and sea-salt.

## SCIENTIFIC OBJECTIVE

This grant incorporated two proposals that have three major efforts. These included support for our participation in and analysis of ASTEX data and a related measurement program at a coastal site in Hawaii with particular emphasis of the relationship of the aerosol variability to the sulfur cycle. A more recent proposal funded under this same grant number calls for the development of an ammonia flux detector for the real time study of ocean-atmosphere fluxes.

The measurements proposed under the first two efforts mentioned above are designed not only to provide information on the size and concentration of the atmospheric aerosol but also to measure size dependent properties of the aerosol that we have found to be related to both its chemistry and optical effects. For many remote regions, the submicron aerosol mass is usually dominated by a mix of sulfuric acid or sulfate. The difference in thermal volatility of sulfuric acid, ammonium sulfate and other refractory constituents such as soot, salt, and dust can be used as means to identify the presence and concentration of these species. Rapid-response optical counting and sizing instrumentation coupled with thermal decomposition is used to obtain size resolved information on the aerosol volatility. This behavior is used to infer the relative concentrations of the various species present in the aerosol. Our intent is to carry out measurements and analysis that can quantitatively link the variability in the concentrations of these species (particularly sulfate) in the marine boundary layer to the aerosol optical properties.

Ammonia is the most common natural base that neutralizes aerosol sulfate it can have important implications for aerosol composition and related optical properties. Because our measurements and those of others indicate that oceanic emissions of ammonia can be significant and because existing techniques for measuring the flux are both slow and prone to errors we developed continuous "potential" ammonia flux system. We refer to it as "potential" since the

measurement is made in an enclosed chamber with prescribed conditions and has to be scaled for ambient conditions of wind speed, temperature etc. The goal will be to determine the ammonia flux from surface waters continuously with temporal resolution of about 30 minutes or less. The device will be built and tested as a prototype of a device suitable for shipboard deployment.

**APPROACH**

We have used rapid measurement techniques that can resolve the small scale variations in aerosol properties in response to variable sources and process. These are integrated to into a system that allows us to explore the links between aerosol physico-chemical processes and their optical effects as well as those that influence the formation, growth and evolution of the aerosol.

1) Use a thermally conditioned optical particle counter to determine the size distribution of sulfur aerosol including the relative neutralization of the submicron sulfur mass by inferring the NH4+/SO4= ratio.

2) Measure the concentration and volatility of condensation nuclei with diameters above 0.02 $\mu$m using a differential mobility analyzer, DMA. These are typically the subclass of atmospheric nuclei that are most efficient as cloud condensation nuclei (CCN).

3) Measure the CN remaining after heating to 300°C. Such refractory particles in the atmosphere are surface derived. These are either soot, sea-salt or dust, and can be dominated by continental contributions. Hence, they are a separate subclass of CN that can vary independently from the total CN. We find the ratio of the heated to unheated CN to be a clear indicator of air mass character that tends to be high for continental and combustion sources but low in cleaner marine air.

4) Measure the ultrafine particles in the size range of 0.02 to 0.003 $\mu$m. that are identified by the difference between the TSI 3025 and TSI 3760 CN counts. These particles have a short atmospheric lifetime due to loss by diffusion to existing surfaces (larger aerosol etc.). High concentrations in the atmosphere often indicate in-situ production of new aerosol by homogeneous nucleation.

5) Carry out continuous aethaelometer (soot) measurements in order to assess the concentration of soot present in the air mass as an indicator of aerosol from anthropogenic emissions or biomass burning.

6) Monitor cloud condensation nuclei spectra at our coastal site in order to establish relationships between the aerosol physicochemistry identified above and the CCN spectra activated in clouds.

7) Carry out sun photometer measurements (in cooperation with Dr. Nels Laulainen, Battelle Northwest) of aerosol optical depth for comparison to our in-situ aerosol microphysics.

8) Carry out continuous integrating nephelometer measurements at ambient conditions in order to validate the in-situ aerosol optical properties derived from our microphysical measurements.

The above measurements provide various evaluations of the aerosol properties that are related to its chemistry, source regions, transformation properties and optical effects. Our objectives have been focussed upon an intensive analysis of the ASTEX data set but also include the establishment of a time series of size resolved aerosol microphysical measurements in the Central Pacific MBL. Microphysical data was used to model EO properties in the MBL and compared to measurements of MBL spectral optical depth.

## TASKS COMPLETED OR TECHNICAL ACCOMPLISHMENTS

This year we finalized the analysis and two papers (see below) related to the above objectives. These grew out of our participation in the ASTEX experiment appeared in a special JGR issue dedicated to that experiment. Another major effort was expended upon the deployment of a portable aerosol research laboratory at a coastal site in Hawaii in order to study and link the physical, chemical and optical properties of boundary layer aerosol. Specific activities follow:

* Used measured aerosol physics and chemistry during vertical profiles to establish and model optical properties of aerosol that included an optical extinction/radiative closure experiment during ASTEX with in situ Total Diffuse and Direct Radiometer (F. Valero - NASA/AMES).

* Carried out analysis and modeling of Lagrangian aerosol evolution experiment and published JGR paper on modeling during Lagrangian 2 of ASTEX.

* Submitted paper on characterization of clean air and polluted aerosol fields during ASTEX.

* Carried out aerosol measurement and radiative measurements at coastal sites in Hawaii for two month period. Included instrument development and calibration.

* A light weight instrument package suitable for deployment on a Cessna 172 was assembled, tested and deployments were made of the north coast of the Big Island of Hawaii.

* A prototype ammonia flux instrument was constructed and preliminary tests carried out. A masters theses will be completed on this instrument in spring 1997.

## SCIENTIFIC RESULTS

* Demonstrated that modeling of aerosol microphysics could be successful at establishing radiative closure with in-situ aircraft measurements within about 20%. Confirmed that experimental techniques are sound and that closure is possible. Our results also showed that fine particle sulfate dominates short wavelength extinction for pollutant aerosol over the Atlantic.

* Demonstrated that soot aerosol in European pollution was internally mixed with sulfate and contributed about 15% to the total column extinction.

* Demonstrated that a Lagrangian aerosol experiment was feasible and that the dominant influence on aerosol evolution in a non-precipitating system was dilution through entrainment from the free troposphere. We have demonstrated for the first time that we are aware of the use of aerosol evolution and a decouple boundary layer model to establish constraints on entrainment through the inversion and mixing through the decouple layer.

* Demonstrated that and automated ammonia flux detector is feasible and can be deployed from ship under typical open ocean conditions.

## SIGNIFICANCE

The results of our linking aerosol microphysics to optical properties and the experimental approach used during ASTEX provide the kind of measurement and modeling linkages that can be used to model aerosol properties to their radiative effects. This information can also be used to validate and refine operational optical models such as NOVAM. Continued application of this approach to our data in the clean central Pacific including the coastal and breaking wave environment will should provide new inputs for regimes where the NOVAM model has less reliability.

Our paper demonstrating the significance of entrainment through the inversion to aerosol evolution in the marine boundary layer is expected to create a new awareness of the significance of entrainment to aerosol evolution and boundary layer processes. This awareness has already contributed to the success of our Christmas Island research program (ONR) and ACE-1 (NSF) by allowing us to model the diurnal dynamics of the aerosol and explore processes that we otherwise would not have identified.

The linkages of aerosol physical, chemical and optical properties being explored during ASTEX and the current Hawaiian coastal measurements by ONR have been expanded under a proposal to NASA that includes column radiative closure experiments and satellite intercomparison and validation based upon in-situ aerosol optical properties. Both activities will help link in-situ and remotely sensed aerosol optical properties that will need to improved modeling of boundary layer aerosol fields.

The prototype ammonia system demonstrated the feasibility of this "potential" flux technique for ship deployment. This technique could dramatically increase the available data on ammonia fluxes in the open ocean. However, further refinement and calibration will be needed before it can be used in a quantitative sense.

## STUDENT MASTERS THESIS - To be completed by 6/97

Direct Measurement of a Potential Ammonia Flux from Seawater with a Gas Diffusion System by Tomoe Uehara

**PUBLICATIONS**

P Clarke, A.D., J.N. Porter and F. Valero and P. Pillewski, Vertical profiles, aerosol microphysics and optical closure during ASTEX: measured and modeled column optical properties, accepted JGR 10/95.

P Clarke, A.D., T. Uehara and J.N. Porter, Lagrangian Evolution of an Aerosol Column During ASTEX, accepted JGR. 10/95

PS Clarke, A.D., T. Uehara and J.N. Porter, Atmospheric Nuclei and Related Aerosol Fields over the Atlantic: Clean Subsiding Air and Continental Pollution During ASTEX. submitted to JGR, responding to reviewers.

PS Porter, J.N. and A.D. Clarke, An Aerosol Size Distribution Model Based upon In Situ Measurements: Aerosol Backscatter Calculations, submitted to JGR Atmospheres,(responding to reviewers).

PS Porter, J.N., A.D. Clarke and P. Flament, Deriving Optical Depths from Satellite: Validations and Modeling Studies, submitted to JGR Atmospheres, responding to reviewers.

**Presentations**

Clarke, A.D. invited speaker for opening presentation at Gordon Conference in Atmospheric Chemistry, 1995, Salve Regina, R.I.

Clarke, A. D. and J. N. Porter, Aerosol Measurements and Optical Extinction in the Marine Boundary Layer, in Proceedings of the Aerosol and Atmospheric Optics Conference, Snowbird Utah, Sept. 26-30, 1994.

Clarke, A.D., J.N. Porter, F. Valero and P. Pilewskie, Aerosol Measurements and Optical Extinction in the Troposphere, 13th Annual Meeting of the Association for Aerosol Research, UCLA, Aug. 1994.

Clarke A.D. and R. Schnell, Black Carbon Variability in the Pacific Free troposphere and Marine Boundary Layer, 5th International Carbon Conference, Berkeley, CA., Aug. 22-26, 1994.

Porter, J.N. and A.D. Clarke, N. Larson and E. Dutton, "Variable Aerosol Phase Function and Optical Depths Derived from AVHRR Satellite", SPIE Aerospace Science and Remote Sensing (Orlando, October 1993)

Porter, J.N. and A. D. Clarke, "A New Marine Aerosol Model and the Optical Response from Satellite, American Meteorological Society (Nashville, January 1994)

Clarke, A.D. and J.N. Porter, "Aircraft Aerosol Measurements and Optical Properties During ASTEX", American Meteorological Society (Nashville, January 1994)

Uehara, T, A.D. Clarke, P.K. Dasgupta and G. Zhang, Direct Measurement of Potential Ammonia Flux Using a Gas Diffusion System, Fall AGU 1996

Litchy, M. and A.D. Clarke, Light-Aircraft Portable Sampling Package for Measuring Differential AerosolRadiative Properties in the Pacific Marine Boundary Layer, paper 1C2, Annual Conference of American Association for Aerosol Research, Orlando, Oct, 1996.

**PROFESSIONAL RECOGNITION**

Invited speaker for opening presentation at Gordon Conference in Atmospheric Chemistry, 1995, Salve Regina, R.I. 6/95

Appointed to National Research Council Panel on the Atmospheric Effects of Aircraft Emissions (PAEAN), 3/95

Given Tenure as Associate Research Professor at University Of Hawaii, 8/95